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THERMAL DESORPTION CAPABILITY DEVELOPMENT FOR ENHANCED ON-SITE HEALTH RISK ASSESSMENT: HAPSITE® ER PASSIVE SAMPLING IN THE FIELD

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14. ABSTRACT
This report details the results of axial tube-type (diffusion cap) diffusive (a.k.a. passive) sampling with the HAPSITE® ER in comparison to a standard benchtop GC-MS. A series of environmental samples were collected with TD tubes and were analyzed in both GC-MS systems. The benchtop GC/MS performed extremely well compared to theoretical values, even at the extremely low ambient VOC levels present. The ER did not perform as well but demonstrated enough capability that it will meet mission needs at levels typically considered hazardous. Although the HAPSITE® ER did not perform as well as the ISQ, this study does illustrate the utility of passive sampling Recommendations are included that may improve ER performance with passive sampling.

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1.0 EXECUTIVE SUMMARY

The focus of this study was to assess the accuracy of using passive (diffusive) sampling systems with the Hazardous Air Pollutants on Site (HAPSITE)® Extended Range (ER) Thermal Desorption (TD) system for ambient air quality measurement. To accomplish this, passive performance was evaluated by comparing the results obtained from both the HAPSITE® ER and a bench-top Gas Chromatograph-Mass Spectrometer (GC-MS) system (ISQ). Nine sites were sampled and analyzed for compounds using Environmental Protection Agency (EPA) Method TO-17. A method was developed to determine the mass on tube and experimental uptake rate of each compound detected. The reproducibility and accuracy of the triplicate passive calculations for mass on tube is presented.

The ISQ data generated uptake rates for 12 of 18 detected compounds which were within 25% of the ideal (theoretical) uptake rates and/or uptake rates published in literature even though validation procedures were not applied that would have likely increased accuracy further. In contrast, the uptake rates calculated from the HAPSITE® ER were generally much lower than those reported by ISQ and compared to the ideal uptake rates, with only 1 of 15 compounds falling within 25% of the ideal uptake rate. Further analysis and supposition reveal that the sites that were chosen were in local environments where significant exposures to highly hazardous compounds were not expected, and the already low detected concentrations were below HAPSITE limit of detection resulting in higher ambient concentration calculations for each compound and lower uptake rates. Also, since compounds on thermal desorption tubes have different stabilities, less-stable compound concentrations may have been further reduced beyond instrument detection.

Although the HAPSITE® ER did not perform as well as the ISQ, this study does illustrate the utility of passive sampling. After careful examination of the results, this report includes several recommendations which further support passive sampling using the thermal desorption capability of the HAPSITE® ER. Key recommendations are as follows:

- Since this study generally addressed compounds that were present in air, optimization of HAPSITE methods for targeted compounds is recommended,
- To enhance sensitivity, controlled laboratory experiments with spiked TO-15 compounds on blanks should be performed,
- Controlled laboratory analysis of uptake rates for compounds reported in this study (as well as others relevant to the BE field) would be beneficial in further characterizing the field sampling environment, and
- Quantify the degree to which increasing sampling time for passive collection improves HAPSITE® ER results. Published uptake rates include both workplace sampling (eight hours) and environmental sampling (about four weeks) (Markes 2006).

With further developed operational guidance, passive sampling with thermal desorption is clearly a highly sensitive and useful tool in general and when analyzed with the HAPSITE® ER, it can be a viable mechanism for environmental sampling to get exposure assessment in the field, although it will likely need higher challenge concentrations to be effective and well described methods to suit current operational need.

2.0 INTRODUCTION

TD is a sample collection process designed to capture Volatile Organic Compounds (VOCs) by pumping air through a tube containing a sorbent media in an environment where the VOCs are generated. The media in the tube will entrain the VOCs until heated in an analytical instrument where they are released and measured, typically in a GC with an MS detector. The sampling and analytical process requires no hazardous solvents or any of the relatively complex laboratory procedures that go along with solvent extraction methods for Liquid Chromatography-MS (LC-MS). Additionally, TD is approximately 1000X more sensitive, requires minimal sample preparation, and has higher sample recovery than solvent extraction (Bart 2001). The process is also non-destructive so the media and tubes are re-used. TD is a significant improvement over legacy processes because the simplicity of the analysis means that large-scale sample collection and analysis with on-site lab-grade instruments could be widely available to the deployed health risk assessor that has the required equipment available. Air contact with the sorbent is the sole requirement for the media to capture the chemicals so passive (diffusive) sampling is also possible. Passive sampling eliminates the need for calibrated air sample pumps reducing both the logistics tail that goes into maintenance and power for the pumps but also reduces the need for trained operators to be present during the sampling.

The purpose of this report is to determine the effectiveness of passive sampling with standard TD tubes for field analysis in the portable GC-MS system, the HAPSITE® ER, by comparing it to the gold standard bench-top GC-MS. Specifically, we utilize a Thermo ISQ GC-MS in this study, which is referred to as "ISQ" throughout the document. The ER is the newest generation of HAPSITE This capability is attractive because it is easy to deploy in the field which could provide the Bioenvironmental Engineer (BE) a valuable additional tool to perform Health Risk Assessment (HRA)/force health protection in the operational environment. The BE can deploy these passive systems by placing them in the area where toxic vapors are suspected with negligible BE interaction. Passive sampling also allows the BE to place many tubes in replicate in multiple locations within the area to get a better profile of VOC concentrations across the region. In addition, the samplers can be deployed for a period of a few hours to several weeks to get a better idea of the Time Weighted Average (TWA) of the compounds across a given time period or on many individuals at once to develop a population's exposure profile. Active sampling, actively pulling air through the tube with a pump, can concentrate more of the chemical on the media quicker, so low levels can be detected faster. The specifics of passive and active sampling are described in greater detail below.

2.1 Passive/Active Sampling Methods

Figure 1: C describes the three types of sampling considered in this study; the first two methods are passive, and the third is an active pumping procedure. Radial sampling is of interest because of shorter sampling times (one to six hours) (Markes 2012) compared to axial sampling (eight hours-several weeks). Some examples of applications where radial sampling is preferable include monitoring the effects of specific industrial process that change throughout the day, or VOC monitoring for contaminants from changing traffic patterns (Markes 2012). Shorter sample times are due to the fact that the diffusion path is parallel to the radius of the tube, allowing for a higher surface area (23.6 cm^2) and shorter diffusive path length than axial diffusion tubes, resulting in a 100X faster sampling rate (Figure 1: C). The sampling rate limits the practical volatility range of compounds of interest to those with volatilities less than or equal to benzene due to the high risk of back diffusion of radial samplers. Therefore, stronger sorbents are usually

required for radial sampling than for axial or pumped sampling. Additional considerations for radial diffusion include saturation of the sorbent tube due to the higher sampling rate, and since the samplers are relatively new, fewer published uptake rates are available. Following sampling, the sorbent housed within the porous polymer body of radial samplers are manually inserted into stainless steel TD tubes. As reported in the *Evaluation of Potential Accessories to Support the HAPSITE® ER Thermal Desorption Capability* (Kwak, et al.) there were difficulties in early trials with these samplers. There was significant leakage of sorbent media during the handling of the samplers which resulted in sample loss, and accumulation of sorbent media in the portable GC-MS thermal desorber, concentrator, GC column and mass spectrometer, resulting in clogging problems and decreased instrument performance.

Axial passive sampling (Figure 1: C) is ideal in situations where longer term sampling is of interest, or in deployed environments where the power and pumping required for active sampling and benchtop ISQ evaluation may be logistically difficult. In axial sampling, a thermal TD tube is capped at one end, and a diffusion cap is placed over the other end that protects the sorbent material from variations in environmental air flow and provides a specific diffusion path length and surface area for comparison to a wealth of published data (Markes 2006). Compounds interact with the sorbent through axial diffusion through the diffusion cap. At the conclusion of the sampling period, the TD tubes are loaded directly onto the GC-MS instrument for analysis.

Active sampling has been discussed in detail in the *Evaluation of Potential Accessories to Support the HAPSITE® ER Thermal Desorption Capability* (Kwak, et al.) and the *HAPSITE® ER Field Sampling Report* (Kwak, et al.); however, the design is shown in Figure 1: C. Tubing is used to attach a small pump to the TD tube, and the sample is pulled through the tube at a specified flow rate for a known time period. TD tubes are then capped and returned to the lab for GC-MS analysis. The method is well-validated by the literature and by our labs in previous reports, but it requires well-trained personnel being physically on site during the sampling duration, and pump calibration procedures prior to sampling.

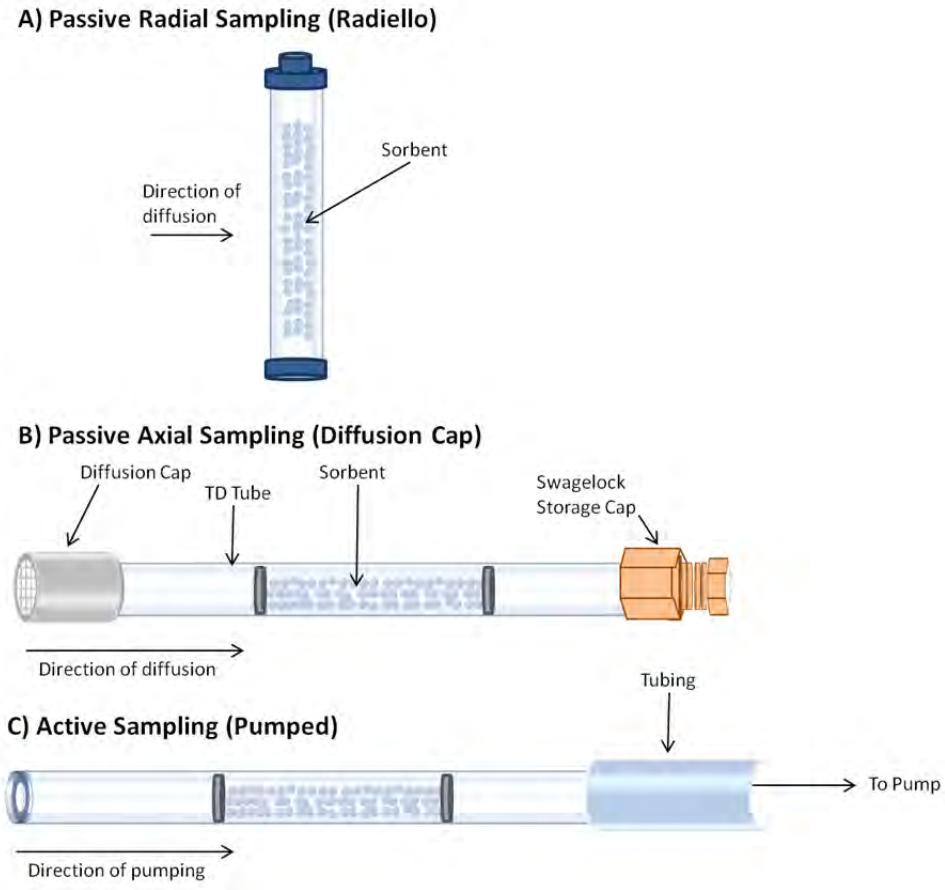

Figure 1: Comparison of Sampling Methods used in this Study

A) Passive radial sampling (Radiello® uses a cartridge but the concept of higher surface area is the same); B) Passive axial sampling; C) Active sampling.

The Inficon HAPSITE® Smart Plus (SP) air sample collection is limited to direct sampling from the instrument which can only be done where the instrument is and done one at a time for usually only a minute of active sampling time for every 20-30 minutes of analysis or via sample bags collected in the field and brought back to it. Bags are very cumbersome to collect and transport (they are fragile), have a very limited storage time before leakage becomes problematic, and can be the source of inaccuracies in analysis due to issues such as condensation or bag contamination. These limitations tend to minimize the use of the sample bags in practice. TD is a capability that Inficon has added to the HAPSITE® ER. The manufacturer recognized the limitation of the HAPSITE® SP and identified a way to greatly expand the user's ability to collect and bring samples back to the instrument for analysis. We have evaluated the potential of TD in general and the HAPSITE® ER's TD capabilities specifically for use within the HRA process.

2.2 Background Information for Primary TD Equipment Studied

2.1.1. Inficon HAPSITE® ER

The HAPSITE is a man-portable GC-MS used to detect, identify, and quantify unknown hazardous materials in operational environments so that it can provide near-real-time, on-site analysis to support operational risk management decisions.

Two versions of the HAPSITE have been manufactured with the SP being the last upgrade to the original model available. The ER is the name of the second generation made by Inificon. The original HAPSITE and the ER are both equipped with a hand-held sampling probe through which air samples are delivered into a concentrator in the HAPSITE system. The HAPSITE® SP is no longer available for purchase since the upgraded version has recently been introduced (Figure 2: H). The HAPSITE® ER has many advantages over HAPSITE® SP. In particular, the newer version can accommodate a Solid Phase Microextration (SPME) accessory and a TD accessory able to desorb VOCs off of samples collected externally, SPME fibers and TD tubes, respectively. The TD tubes are used to concentrate samples, thereby providing an enhanced analytical sensitivity.

In the HAPSITE system, VOCs are brought in through the various sample introduction methods; hand-held probe, headspace analyzer, SPME accessory, TD accessory and are collected onto a concentrator. They are then transferred to and separated by a GC column, passed through a membrane maintained at 80ºC, and into the MS detector while the inorganic gases (e.g. nitrogen and oxygen) are discarded (Sekiguchi et al. 2006). The detector is a quadrupole MS and is operated under vacuum provided by a Non-Evaporative Getter (NEG) and an ion sputter pump (Smith 2012).

Figure 2: HAPSITE® ER *(left)* **and TD Accessory** *(right)*

2.1.2. Stainless Steel (SS) TD Tubes

Inficon's thermal desorption capability on the ER was built with glass tubes. Due to the lack of practicality of using glass tubes in a deployed environment, SS TD tubes (a single component sorbent Tenax® TA were used in this study. The tubes were purchased from Markes International (South Wales, UK). All tubes were conditioned prior to use based on the manufacturers' instructions.

2.1.3. Diffusion Caps with SS TD Tubes

Diffusion caps were purchased from Markes International (South Wales, UK) and are shown in Figure 3. The cap is placed on the sampling end of a Tenax® TA tube while the other end is fitted with a brass cap so that sample collection is self-contained. This means that the sorbent is exposed to the environment only through the diffusion cap, because the other end is closed. This simplifies analysis because all sampling can be considered to occur by diffusion over a single fixed sampling distance, allowing for calculations using the well-studied diffusion constant of a compound.

Figure 3: Diffusion caps

2.1.4. Radiello® Passive/Diffusive Sampling System

The Radiello® is a system that is designed to provide maximal surface area of the collection media to increase efficiency and sensitivity for passive sampling. The radial diffusive sampler Radiello® has more surface area to collect an air sample over axial diffusive samplers. The Radiello® Carbograph 4 adsorbents (RAD145) were purchased from Sigma-Aldrich (St. Louis, MO) and conditioned prior to use based on the manufacturer's instruction. Figure 4 displays the system where the cartridge is placed within the white diffusive body. After sample collection, the cartridge is taken out and placed in an empty stainless steel tube for thermal desorption analysis.

Figure 4: Radiello® Passive/Diffusive Sampling System

The Radiello system proved to be problematic in use leaking material as discussed. Because of this, this system was not evaluated and will not be discussed any further in this report.

3.0 METHODS, ASSUMPTIONS AND PROCEDURES

Passive and active samples were collected at nine field sites. A total of 6 passive and 28 active collocated samples were obtained from each site. The passive samples were opened to the environment for diffusion, for approximately seven hours. The passive samples were split so that three of the passive samples were to be run on the gold standard ISQ GC-MS and the other three would be run on the HAPSITE® ER. The active samples were used to determine the "known" concentrations for the passive samples to be compared. The 28 samples collected were done in duplicate (split samples) in a time series with the LESS™-P, so the total sample time for each event was cut into 14 time slices covered by a set of duplicates of the active tubes. These results were averaged to compare to the passive result. One set of duplicates (14 tubes) was analyzed on the ISQ and the other set was analyzed on the HAPSITE® ER. A single blank thermal desorption tube was carried onto the site and left with the equipment but was only opened instantaneously and then closed again.

3.1 Logistically-Enabled Sampling System (LESS)™-P Time-Series Sampling System

The LESS™-P (Signature Science, Austin, TX) time-series TD tube sampling system shown in Figure 5 is a self-contained air pumping system that allows for the installation of 28 TD tubes into its manifold and controls the flow so that sampling can be performed through each tube sequentially.

Figure 5: LESS™-P Time Series Sampler

Fourteen time-series TD tubes were collected over the entire sampling period so that passive calculations could be accomplished. Ideally, one needs to know the time-weighted average of the concentration of each compound present in the atmosphere at each sampling site during the same time period of passive sampling. Samples were collected in time series at 30 mL/min for 30 minutes for a total volume of 900 mL for each TD tube.

3.2 HAPSITE® ER

The HAPSITE® ER system was purchased from Inficon Inc. (East Syracuse, NY) and the performance of a single instrument was evaluated in this study. A thermal desorber was attached to each HAPSITE where a non-polar column (100% polydimethylsiloxane; 15 m×0.25 mm ID ×1.0μm df) was equipped. The temperatures of column, membrane, valve oven and heated lines were 50, 80, 70 and 70ºC, respectively. The temperature of the thermal desorber was set to 330ºC,

but the actual temperature of SS sorbent tubes only reached around 200ºC. The desorption time was 10 min. The GC temperature program started at 50°C for 2 min, increased at 3°C/min to 80°C, at 12°C/min to 120°C, and at 26°C/min to 200°C where the final temperature was held for 5.6 min. The GC analysis time was 24 min. Nitrogen was used as the carrier gas at a constant pressure mode of 88 kPa. The mass spectrometer was operated in the electron impact ionization mode at 70 eV. The mass scan range was m/z 41 to m/z 300 and the scan time was 0.78 sec. HAPSITE injects known volumes of internal standards bromopentafluorobenzene and 1,3,5-tris(trifluoromethyl)benzene (5.44 ppm and 10.83 ppm, respectively) for each analysis from the internal standard canister obtained from Inficon.

For the HAPSITE® ER calibration curves, Tenax SS tubes with different concentrations of TO-15 standard mixture were prepared: 0.5, 1, 2, 5, 25, 50 and 100 ppbv based on a total volume of 400 mL. Several replicates at each concentration were prepared to obtain a validated calibration curve plotting peak height versus concentration. Peak heights were found using a manual data analysis method rather than relying on the HAPSITE® ER supplied software due to concerns related to compound coelution and misidentification (described in *HAPSITE® ER Field Sampling Report* (Kwak, et al.)). The samples were analyzed using the HAPSITE® ER thermal desorber and were quantified using the calibration curve developed to determine concentration collected. Since many replicates are applied to the HAPSITE® ER calibration curves, a correction factor was used to minimize resource consumption. Therefore, each concentration was calculated by applying the 400 mL calibration curve and multiplying by the correction factor (900/400= 2.25) to obtain the concentration in 900 mL total sample volume for this study.

3.3 Thermo ISQ GC-MS

To evaluate and validate the thermal desorption capability of HAPSITE® ER, duplicate sorbent tubes were prepared: one was analyzed by HAPSITE® ER and the other by Thermo ISQ GC-MS. The Thermo GC-MS utilized a modified version of EPA Method TO-17 for monitoring VOCs via automated, cryogen free thermal desorption using a TD-100 thermal desorber (Markes International, South Wales, UK) in line with a Trace GC Ultra and ISQ single quadrupole mass spectrometer (Thermo Scientific, Waltham, MA). The TD-100 parameters are as follows: tube desorption temp.: 310°C; tube desorption time: 10 min; flow path temp.: 160°C; trap flow: 50 mL/min; pre-trap fire purge time: 1 min; trap low temp.: 25°C; trap high temp: 315°C for 5 min; trap heating rate: 40°C/s (MAX); Split ratio: 3.5:1 (outlet (trap) split only). A TG-624 column (60 m x 0.32 mm ID x 1.80 μm df; Thermo Scientific, Waltham, MA, USA) was installed into the GC. The GC temperature program started at 40°C for 1 min, and increased at 10°C/min to 240°C where the final temperature was held for 20 min. The GC analysis time was 41 min. Helium was used as the carrier gas at a constant flow of 2 mL/min. The mass spectrometer was operated in the electron impact ionization mode at 70 eV. The transfer line temperature was 230°C and the ion source temperature was 275°C. The mass scan range was m/z 35 to m/z 300 and the scan time was 0.154 sec.

Tenax SS tubes were used to prepare the calibration curve using 2, 10, 25, 50 and 100 ppbv with TO-15 standard mixture at 900 mL total volume. TraceFinder™ software produces a calibration curve automatically for each compound by integrating peak area and plotting the response factor of each compound relative to the internal standard at each concentration. The software also allows the operator to set concentration levels directly to compensate for variability in calculated calibration curve concentrations.

3.4 Passive Sampling Techniques

Passive sampling was accomplished with the use of a diffusion cap on one end of the stainless steel Tenax® TA tubes with the other end capped by a brass end cap. Samples were analyzed on the HAPSITE® ER and Thermo ISQ GC-MS.

The mass on tube was calculated for each detected compound using the ideal gas law in both the sampled tubes and a trip blank. The trip blank is a tube that is co-located with the sample tubes, but is briefly opened to simulate the addition of the diffusion cap to sampling tubes, then recapped during the sampling period. This simulates any compound that adsorbs due to the removal of the storage cap in the short time period before the diffusion cap is added. Equation 1 was used to calculate the experimental uptake rates (mL/min):

$$UR = \frac{(m - m_{b)}}{c} \times t^{-1} \quad (1)$$

Where m is the mass (µg) calculated from the passive diffusion tube following GC-MS analysis (average of three passive measurements), m_b is the calculated mass of the chemical on the trip blank, c is the background-subtracted time-weighted average of the chemical determined by LESS-P sampling over the entire time course of the passive measurements (µg/L), and t (min) is the passive sampling time period (Maddalena, 2013). See Table 1 for passive sampling collection times. The background subtracted concentration was determined by Equation 2:

$$c = \frac{(m - m_b)}{V} \quad (2)$$

The ideal uptake rates (mL/min) were calculated according to Equation 3 (Markes 2012):

$$U_{ideal} = \frac{60 * DA}{Z} \quad (3)$$

Where D is the diffusion coefficient of the compound in cm^2/sec (http://www.gsi-net.com/en/publications/gsi-chemical-database.html), A is the cross sectional area of the sampling tube (0.191 cm^2, Markes 2012), and Z is the path length of the air gap (1.5 cm, Markes 2012).

Table 1: Passive Collection Times for Each Site (ISQ and HAPSITE)

Table 1. Passive Collection Times for Each Site (ISQ and HAPSITE)	
Site	Total Min
Auto Hobby Shop	429
C17 Hanger	405
Bowling Alley	420
Gas Pumps	456
Hanger 445	423
Restoration	420
Pest Mgmt	420
Vivarium	420
Microbiology	420

3.5 Passive Sampling Data Analysis

The LESS™-P data was quantified on ISQ by fitting the data from each compound to a calibration curve with a minimum concentration of 2 ppbv. This calibration curve was designed to predict the initial concentration of each compound in the atmosphere sampled using active pumping by mimicking concentrations that would be sampled at 900 mL volume at a known flow rate. Therefore, it does not accurately apply to passive sampling where a mass of compound accumulates by diffusion over a longer time period (approximately eight hours in this study). This means that passive sampling cannot quantify initial concentration, but it can be used to qualitatively compare the ISQ concentrations to LESS™-P and the trip blank in the context that a higher concentration of sample in passive v. trip blank will correlate to an increased mass of the compound adsorbed on the tube.

The study only included compounds with values above the Limit of Reporting (LOR) of 2 ppbv for passive, LESS™-P, or active pump sampling (discussed in previous reports, but not part of this study). If a compound was present above the LOR for any of the sampling methods (passive, LESS™-P, or active), the reported concentrations of that compound for the other sampling methods were included for comparison even if they were lower than 2 ppbv ("reporting criteria"). So even though the active data was not used in this work, if a compound was above the LOR in the active sampling, LESS™-P and passive values were included regardless of whether they were above 2 ppbv for the sake of direct comparison of methods, and method similarity to previous reports.

In this work, compounds considered present by the criteria above (above LOR, or above LOR for any of the sampling methods) were not reported as present in Table 2 (in Section 4.0) if one or more of 4 conditions were met, termed "exclusion criteria." First, if the reported concentration of the passive sampling was less than or equal to that of the trip blank, the compound was considered a tube artifact instead of a valid compound detected. We established a threshold cutoff, where even if one method detected the compound above 2 ppbv, the compound was not reported if the concentration was below 0.05 ppbv. This threshold was used as a subjective cutoff point where instrument operators determined that a compound could no longer be reliably identified from the MS data. Data was excluded if the standard deviation of the triplicate passive tubes was greater than the mean. This introduces doubt into the validity of the measurements due to experimental artifacts, especially since only one trip blank was analyzed (no standard

deviation of trip blank for comparison). Similarly, compounds were excluded if the value of the standard deviation subtracted from the mean of the passive was less than that of the trip blank. This implies that at least one of the triplicate samples is in doubt of being a real detection event.

4.0 RESULTS AND DISCUSSION

4.1 Bench-top GC-MS Passive Results (ISQ)

Of an initial 81 compounds from the 9 sites that were reported to meet the criteria of active, passive, or LESS-P concentration > 2 ppbv, 26 compounds were excluded due to the exclusion criteria. Table 2 details all 56 reports from the 9 sampling sites with standard deviation of the mass calculated for each triplicate measurement. Table 3 summarizes the data by compound for each of the 9 sites, with published uptake rates included for comparison. Overall, 12 of the 18 compounds detected generated uptake rates ±25% of the calculated ideal uptake rates using ISQ. Note that there is a specific process to validate uptake rates experimentally, which involves controlled lab experiments and field sampling (Markes 2009). Uptake rates will vary based on a number of factors including temperature, humidity, exposure time, concentration, etc. They may also differ in the field as a compound competes for adsorption sites on the sorbent with a mixture of other compounds, or they may undergo chemical reactions with other chemicals or inorganic gas species. As such, we compare the experimental uptake rates from this study to the ideal and published uptake rates as a validation of the methods, using a window of ±25%) due to the variability of the conditions of our studies with the published validated uptake rates. Results are presented as passive collection method validation rather than validated uptake rates due to the fact that the full set of recommended controlled lab experiments were not performed in varying conditions.

Of interest, tetrahydrofuran met the reporting criteria for LESS™-P and/or active sampling for 8 of nine sites, but was not reported for passive sampling due to the exclusion criteria (not significantly higher than blank values). 1,4-dioxane met reporting criteria for all 9 sites, but the triplicate passive data were extremely variable in standard deviation (%CV= 67% for the 9 sites) such that only 2 sites passed the exclusion criteria. In comparison, compounds that were detected in multiple sites with uptake rates within ±25% of the calculated ideal uptake rate generally demonstrated lower %CV values: toluene (%CV= 13.4%), acetone (%CV= 23.0%), isopropyl alcohol (%CV= 5.4%). Benzene behaved similarly such that 4/8 passed the exclusion criteria, however the experimental uptake rate was almost 5X higher than the ideal uptake rate. This can be explained in that benzene is not recommended for Tenax® TA because its high volatility can lead to displacement by non-polar high molecular weight compounds (Martin 2010). Benzene and toluene are derived from the sorbent material, and our previous reports have shown a high variability of both detected between tubes. Also, the volatility of hexane and benzene has been reported to be difficult at low exposure doses (<40 ppm/min) in tube-type diffusion samplers due to a change of uptake rate over time (Roche 1998). This explains why the reported hexane uptake rate is 61% of the ideal, but is ~75% of the published uptake rate. Styrene was only reported at one site, which may account for the variability from the ideal value. Previous reports have detailed the challenges of reproducibility detecting styrene (Batterman, 2002; Harper, 2000). The other compounds detected in Table 3 have ratios of experimental/calculated (ideal) uptake rates and/or experimental/published uptake rates within 0.25. This validates passive sampling as a viable reporting method within our lab using ISQ GC-MS.

Table 2: Data Summary by Site (ISQ)

Table 2. Data Summary by Site (ISQ)

Site	Chemical	Average Mass (ng)	SD Passive	Uptake Expt'l (mL/min)	Uptake Calc'd (mL/min)
445hangar	Acetone	9.993	1.931	0.892	0.947
445hangar	Ethyl acetate	1.891	0.604	0.574	0.558
445hangar	Toluene	1.235	0.161	0.459	0.665
Auto Hobby	1,2,4-trimethylbenzene	2.034	0.100	0.449	0.475
Auto Hobby	1,3,5-trimethylbenzene	2.566	0.094	0.452	0.474
Auto Hobby	1,4-dioxane	1.914	1.274	1.113	1.757
Auto Hobby	4-Ethyltoluene	7.825	0.723	0.498	0.542
Auto Hobby	Acetone	7.306	1.407	0.659	0.947
Auto Hobby	Benzene	3.851	0.334	0.547	0.672
Auto Hobby	Cyclohexane or 3-methylhexane	3.829	0.058	0.450	0.599
Auto Hobby	ethylbenzene	5.803	0.088	0.522	0.573
Auto Hobby	Heptane	6.108	0.315	0.433	0.500
Auto Hobby	Isopropyl Alcohol	2.553	0.092	0.821	0.733
Auto Hobby	m,p -xylene	22.189	0.728	0.618	0.535
Auto Hobby	Methyl Isobutyl Ketone	0.777	0.011	0.443	0.573
Auto Hobby	n-hexane	11.666	0.262	0.521	1.528
Auto Hobby	o-xylene	7.166	0.156	0.526	0.665
Auto Hobby	Toluene	24.316	0.966	0.651	0.665
Bowling Alley	Acetone	6.888	2.037	0.484	0.947
Bowling Alley	Isopropyl Alcohol	6.169	0.160	0.444	0.733
C-17	Acetone	9.686	0.811	0.473	0.947
C-17	Ethyl acetate	0.359	0.031	0.256	0.558
C-17	Isopropyl Alcohol	2.212	0.192	0.423	0.733
C-17	Toluene	1.698	0.113	0.395	0.665
Gas Pumps	Acetone	8.245	2.647	0.934	0.947
Gas Pumps	n-hexane	2.292	0.160	0.382	1.528
Gas Pumps	Toluene	1.777	0.230	0.427	0.665
Micro Quan	Acetone	12.257	4.033	0.969	0.947
Micro Quan	Isopropyl Alcohol	65.538	2.257	0.820	0.733
Micro Quan	o-xylene	0.046	0.016	0.704	0.665
Micro Quan	Toluene	0.790	0.301	1.335	0.665
Pest Quan	4-Ethyltoluene	5.196	2.846	0.522	0.542
Pest Quan	Acetone	11.827	4.522	0.891	0.947
Pest Quan	ethylbenzene	2.346	0.885	0.463	0.573
Pest Quan	Heptane	1.490	0.202	0.397	0.500
Pest Quan	Isopropyl Alcohol	1.531	0.135	0.472	0.733
Pest Quan	m,p -xylene	9.290	3.835	0.482	0.535
Pest Quan	n-hexane	2.841	0.309	0.350	1.528
Pest Quan	o-xylene	2.844	0.963	0.443	0.665
Pest Quan	Toluene	16.345	3.217	0.448	0.665
Restoration	1,4-dioxane	9.481	1.626	8.889	1.757
Restoration	Acetone	15.339	2.425	1.018	0.947
Restoration	Benzene	6.800	0.832	5.943	0.672
Restoration	Isopropyl Alcohol	1.365	0.122	0.883	0.733
Restoration	n-hexane	0.298	0.054	0.228	1.528
Restoration	Toluene	5.048	0.151	0.522	0.665
Vivar Quan	Acetone	9.553	1.131	1.060	0.947
Vivar Quan	Benzene	5.753	0.153	3.450	0.672
Vivar Quan	ethylbenzene	9.126	0.227	0.122	0.573
Vivar Quan	Isopropyl Alcohol	16.438	0.317	0.408	0.733
Vivar Quan	m,p -xylene	36.396	1.550	0.413	0.535
Vivar Quan	o-xylene	5.369	0.201	0.369	0.665
Vivar Quan	Styrene	1.406	0.795	1.774	0.542
Vivar Quan	Toluene	1.045	0.102	0.831	0.665
Vivar Quan	Trichloroethylene	2.663	0.647	ND	0.604

Table 3: Compound Data Average Over All Sites (ISQ)

Table 3. Compound Data Average Over All Sites (ISQ)

Compound	# Sites	Average Mass (ng)			Avg. Uptake Expt'l (mL/min)			Uptake Calc'd (mL/min)	Expt'l/Calc'd	Published Uptake Rate (mL/min)	Expt'l/Published
1,2,4-trimethylbenzene	1	2.034	±	ND	0.449	±	ND	0.475	0.95	0.482	0.932238
1,3,5-trimethylbenzene	1	2.566	±	ND	0.452	±	ND	0.474	0.95	0.482	0.936767
1,4-dioxane	2	5.697	±	5.351	5.001	±	5.498	1.757	2.85		ND
4-Ethyltoluene	2	6.510	±	1.859	0.510	±	0.017	0.542	0.94	0.450	1.133252
Acetone	9	10.122	±	2.672	0.820	±	0.224	0.947	0.87		ND
Benzene	3	5.468	±	1.495	3.313	±	2.701	0.672	4.93	0.407	8.141254
Cyclohexane or 3-methylhexane	1	3.829	±	ND	0.450	±	ND	0.599	0.75	0.383/0.361	1.17/1.24
Ethyl acetate	2	1.125	±	1.083	0.415	±	0.225	0.558	0.74	0.444	0.935197
ethylbenzene	3	5.758	±	3.390	0.369	±	0.216	0.573	0.64	0.461	0.799635
Heptane	2	3.799	±	3.265	0.415	±	0.025	0.500	0.83	0.430	0.965028
Isopropyl Alcohol	7	13.687	±	22.162	0.610	±	0.215	0.733	0.83		ND
m,p -xylene	3	22.625	±	13.558	0.504	±	0.104	0.535	0.94	0.419	1.203722
Methyl Isobutyl Ketone	1	0.777	±	ND	0.443	±	ND	0.573	0.77	0.417	1.063363
n-hexane	4	4.274	±	5.048	0.370	±	0.120	0.611	0.61	0.496	0.745943
o-xylene	4	3.856	±	3.098	0.511	±	0.144	0.665	0.77	0.419	1.218657
Styrene	1	1.406	±	ND	1.774	±	ND	0.542	3.27	0.470	3.77417
Toluene	8	5.962	±	8.879	0.760	±	0.318	0.665	1.14	0.512	1.484869
Trichloroethylene	1	2.663	±	ND	ND	±	ND	0.604	ND		ND

4.2 HAPSITE® ER Passive Results

For the nine sites evaluated, one site's data was lost on the ER because there is a limit to the data storage capacity of the instrument that was not previously known. Of the eight sites that data was available, 60 compounds passed the reporting criteria for passive or LESS-P concentration > 2 ppbv, and 6 compounds were excluded due to the exclusion criteria. Table 4 details all 54 reports from the 8 sampling sites with standard deviation of the mass calculated for each triplicate measurement. Table 5 summarizes the data by compound for each of the 8 sites, with published uptake rates included for comparison. 1,4-dioxane, benzene, and styrene values were significantly higher than the ideal uptake rates, similar to the ISQ results. However, the majority of uptake rates calculated by HAPSITE were much lower than those expected by calculating the ideal uptake rate, and only that of cyclohexane/3-methylhexane was within a 25% window of the ideal. Isopropyl alcohol was within 30% of the ideal uptake rate. In depth analysis of the data is provided in the next section.

Table 4: Data Summary by Site (HAPSITE)

Table 4. Data Summary by Site (HAPSITE)

Site	Chemical	Average Mass (ng)	SD Passive	Uptake Expt'l	Uptake Calc'd
445Hangar	1,4-Dioxane	5.635	1.561	1.163	1.757
445Hangar	Acetone	30.365	18.953	0.579	0.947
445Hangar	m,p-xylene	2.174	0.153	0.308	0.535
445Hangar	Toluene	5.313	0.097	0.479	0.665
AutoHobby	1,2,3-trimethylbenzene	4.577	0.026	0.440	0.474
AutoHobby	1,3,5-trimethylbenzene	4.037	0.022	1.861	0.474
AutoHobby	4-ethyl toluene	1.153	0.027	0.196	0.542
AutoHobby	Acetone	12.357	2.718	0.406	0.947
AutoHobby	Cyclohexane or 3-methylhexane	1.094	0.050	0.472	0.599
AutoHobby	ethylbenzene	2.376	0.013	0.305	0.573
AutoHobby	Heptane	2.991	0.024	0.160	0.500
AutoHobby	Isopropyl Alcohol	19.119	0.600	0.777	0.733
AutoHobby	m,p-xylene	2.747	1.671	0.225	0.535
AutoHobby	Methyl Isobutyl Ketone	6.806	0.107	1.056	0.535
AutoHobby	n-hexane	10.244	0.185	0.242	0.611
AutoHobby	o-xylene	1.408	0.049	0.192	0.665
AutoHobby	Styrene	2.555	0.095	1.286	0.542
AutoHobby	Toluene	11.007	0.110	0.378	0.665
Bowling Alley	Acetone	11.309	2.606	0.418	0.947
Bowling Alley	Isopropyl Alcohol	65.015	2.588	0.584	0.733
C17	4-ethyl toluene	2.116	0.001	2.105	0.542
C17	Acetone	15.340	1.644	0.277	0.947
C17	Benzene	8.569	0.289	1.416	0.672
C17	Isopropyl Alcohol	7.749	0.623	0.328	0.733
C17	Styrene	2.748	0.019	0.507	0.542
C17	Toluene	4.963	0.006	0.405	0.665
GasPumps	Heptane	2.797	0.049	0.167	0.500
GasPumps	n-Hexane	3.848	0.085	0.165	0.611
GasPumps	Toluene	7.746	0.054	0.200	0.665
Micro	1,4-dioxane	5.783	0.087	4.023	1.757
Micro	Acetone	9.191	0.099	0.120	0.947
Micro	Benzene	8.726	1.169	0.632	0.672
Micro	Isopropyl Alcohol	83.990	4.483	0.373	0.733
Micro	m,p -xylene	5.843	0.234	0.264	0.535
Micro	o-xylene	0.772	0.059	0.152	0.665
Micro	Toluene	13.331	0.214	0.259	0.665
Pest Mgt	1,2,3-trimethylbenzene	2.818	1.232	0.279	0.474
Pest Mgt	1,4-Dioxane	5.785	0.092	8.609	1.757
Pest Mgt	4-Ethyltoluene	2.930	0.056	0.650	0.542
Pest Mgt	Acetone	16.202	2.545	0.598	0.947
Pest Mgt	Benzene	8.719	1.172	0.815	0.672
Pest Mgt	Ethylbenzene	1.620	0.105	0.262	0.573
Pest Mgt	Heptane	3.453	0.093	0.298	0.500
Pest Mgt	Hexane	4.585	0.265	0.464	0.500
Pest Mgt	Isopropyl Alcohol	0.874	0.413	0.212	0.733
Pest Mgt	m,p-xylene	2.917	0.115	0.166	0.535
Pest Mgt	o-xylene	0.772	0.060	0.155	0.665
Pest Mgt	Toluene	13.343	0.216	0.272	0.665
Vivarium	1,4-Dioxane	5.563	0.545	2.149	1.757
Vivarium	Acetone	13.233	1.868	0.743	0.947
Vivarium	Ethylbenzene	8.197	0.100	0.308	0.573
Vivarium	Isopropyl Alcohol	74.834	4.481	0.946	0.733
Vivarium	m,p-xylene	27.621	0.477	0.328	0.535
Vivarium	o-xylene	2.968	0.126	0.260	0.665

Table 5: Compound Data Average Over All Sites (HAPSITE)

Table 5. Compound Data Average Over All Sites (HAPSITE)

Compound	# Sites	Average Mass (ng)			Avg. Uptake Expt'l (mL/min)			Uptake Calc'd (mL/min)	Expt'l/Calc'd	Published Uptake Rate (mL/min)	Expt'l/Published
1,2,3-trimethylbenzene	3	3.810	±	0.901	0.860	±	0.871	0.474	1.812	ND	ND
1,4-Dioxane	4	5.692	±	0.111	3.986	±	3.302	1.757	2.268	0.000	ND
4-ethyl toluene	3	2.066	±	0.890	0.984	±	0.997	0.542	1.813	0.450	2.186
Acetone	7	15.428	±	6.998	0.449	±	0.211	0.947	0.474	ND	ND
Benzene	3	8.671	±	0.089	0.954	±	0.410	0.672	1.419	0.407	2.344
Cyclohexane or 3-methylhexane	1	1.094	±	ND	0.472	±	ND	0.599	0.788	0.383/0.361	ND
Ethylbenzene	3	4.064	±	3.599	0.291	±	0.025	0.573	0.509	0.461	0.632
Heptane	3	3.080	±	0.337	0.208	±	0.057	0.500	0.417	0.430	0.484
Hexane	3	6.226	±	3.500	0.290	±	0.155	0.61	0.479	0.50	0.585
Isopropyl Alcohol	6	41.930	±	36.767	0.537	±	0.284	0.733	0.732	ND	ND
m,p -xylene	5	8.260	±	10.916	0.258	±	0.065	0.535	0.482	0.419	0.616
Methyl Isobutyl Ketone	1	6.806	±	ND	1.056	±	ND	0.573	1.843	0.417	2.533
o-xylene	4	1.480	±	1.036	0.190	±	0.050	0.665	0.285	0.419	0.453
Styrene	2	2.651	±	0.137	0.896	±	0.550	0.542	1.653	0.470	1.907
Toluene	6	9.284	±	3.811	0.332	±	0.105	0.665	0.500	0.512	0.649

4.3 Comparison of HAPSITE and ISQ Passive Measurements

Direct comparison of the results of the two different instruments should be done with an understanding of the differences of the analysis. For example, HAPSITE is limited in column and desorption temperature of SS tubes compared to ISQ, and the mass scan time is slower, resulting in diminished or elimination of detection capabilities of VOCs with high boiling point or low abundance. Details of this observation can be found in the *Evaluation of Potential Accessories to Support the HAPSITE® ER Thermal Desorption Capability* report. In addition, ISQ employs helium as the carrier gas with a 60 m mid-polar 6% cyanopropylphenyl methylpolysiloxane GC column versus a 15 m mid-polar 100% polydimethylsiloxane (PDMS) with nitrogen as the carrier gas in the HAPSITE® ER column. HAPSITE® ER operates in a constant pressure mode that is not user-adjustable, where pressure is too high for early eluting compounds to separate properly, resulting in coelution of some of the more volatile compounds. Therefore, ISQ should be used as a reference method to compare the analytical results of TO-15 compound detection performance of HAPSITE.

After exclusion criteria, 56 compounds were detected in 9 sites for ISQ data while 60 compounds were reported in 8 sites for the HAPSITE® ER. A total of 18 different compounds were detected in ISQ, while 15 were reported by HAPSITE® ER. Figure 7 shows a comparison of the mass on tube for compounds detected at each of the 8 sites analyzed using both HAPSITE and ISQ. Despite having lower uptake rates for nearly every compound, the actual mass on tube calculated by HAPSITE was generally higher for toluene, isopropyl alcohol, and acetone, and HAPSITE detected 1,4-dioxane more frequently and at higher levels than ISQ.

This variability may be a function of the differences in methods used to calculate the concentrations of compounds detected by ISQ or HAPSITE. ISQ calculation uses a calibration curve for each compound where the area of the peak is integrated by algorithms in the TraceFinder® software. As discussed in the *HAPSITE® ER Field Sampling Report* , the HAPSITE IQ software occasionally misidentifies compounds, and in doing so, the quantifying ion will be incorrect causing the peak area to be misreported. The operators therefore, opted to perform a more manual analysis of HAPSITE data. In this method, the peak height of compounds in the calibration curve are used to build a calibration curve rather than peak area

because the peak area is difficult to accurately define without operator bias since peak fitting algorithms are not available. Also, peak height enables one to accurately quantify two peaks that are not baseline resolved, but that have some overlap at the median. Therefore, while peak height still causes a degree of variability in calibration curves, the manual method was preferred over the HAPSITE IQ software because peaks were not misidentified. One problem with this manual method is that co-eluting compounds cannot be differentiated because the quantifying ion is not used to determine the peak profile of the individual compounds. This will lead to variability where compounds co-elute, such as acetone, isopropyl alcohol, ethanol, and pentane. The *HAPSITE® ER Field Sampling Report* also noted difficulty in quantifying hexane with HAPSITE compared to ISQ, as the concentrations are typically reported as lower in the HAPSITE® ER.

Another potential for error lies in the operator observation that concentrations above ~25 ppbv were not accurate for HAPSITE. This may be a function of exceeding the upper limit of the working experimental range of the HAPSITE® ER for the methodology used in this study. Experiments are currently underway to gauge the quantitative performance characteristics of the instrument. Also, the highest concentration tested on the calibration curve was 100 ppbv, and some of the compounds either saturated somewhere in the range tested, or demonstrated nonlinear curves.

HAPSITE® ER also differs from ISQ in the sensitivity of the HAPSITE to calculate the concentration of trip blank. HAPSITE appears to report a zero value for any concentration below ~0.1 ppbv in the processed data files. This is a fundamental problem of the HAPSITE instrument itself, as it does not detect any peak below this level. If this value is falsely lower than what should be reported, the m_b (blank mass on tube) term in equation 2 will be lower than the actual concentration, causing a falsely high calculation of the ambient concentration of the compound, in turn leading to a lower uptake rate calculated by equation 1. Most of the trip blank values for all compounds were in the 0.1-1.5 ppbv range, which may be below or in the area of the limit of detection of the instrument. This characteristic is expected to be a major contributor to the deviation of the HAPSITE uptake rates from the ideal uptake rates, typically trending lower than expected. This factor is expanded upon in Section 4.4.

4.4 Statistical Analysis of Data

The distribution of concentrations relative to the blank was analyzed (Figure 6) to attest signal from background. Overall, we observed a bimodal population that we argue is made up of true and null effects, respectively; in our study design we reported the compound concentration if there was a detection in any sampling periods, and hence, the dataset is expected to comprise several null effects; the bimodal presence supports this assertion. Based upon these measurements, a value of 3.64X higher than that of the trip blank was recommended to ensure a type I error rate of 5% (for ISQ); critical value was derived by taking 5% area under null effect curve. This amount is not practical, but a value even 2X higher than the trip blank was associated with 45% type I error rate; critical value was derived by taking 45% area under null effect curve; additional replicates in either trip blank or active sampling may lower the variance in the null effect curve, and hence, allow for a more liberal critical value. Therefore, we recommend dispensing the trip blanks in replicate as well as the passive sampling tubes to account for tube-to-tube variability of compounds. The goal is to ensure that any compound that is considered reportable is actually present, and not merely an artifact of the tubes. An initial

study deploying many trip blanks (10+) would give a good indication of how many trip blanks should be used in future studies.

To summarize this section in non-statistical language, based on our results, we would need to observe a concentration 3.64X higher for a given compound in a field sampling tube than the concentration of the same compound in the blank tube to feel confident that the compound was actually present at the sampling site rather than an artifact of the blank tube. This value is not practical, so employing either multiple trip blanks to analyze at each site, or further characterizing the composition of the tubes would provide a better estimate of the variability of the tube artifacts. In turn, this increased confidence would drive down how much higher the sample concentrations should be compared to the blank value for a given compound.

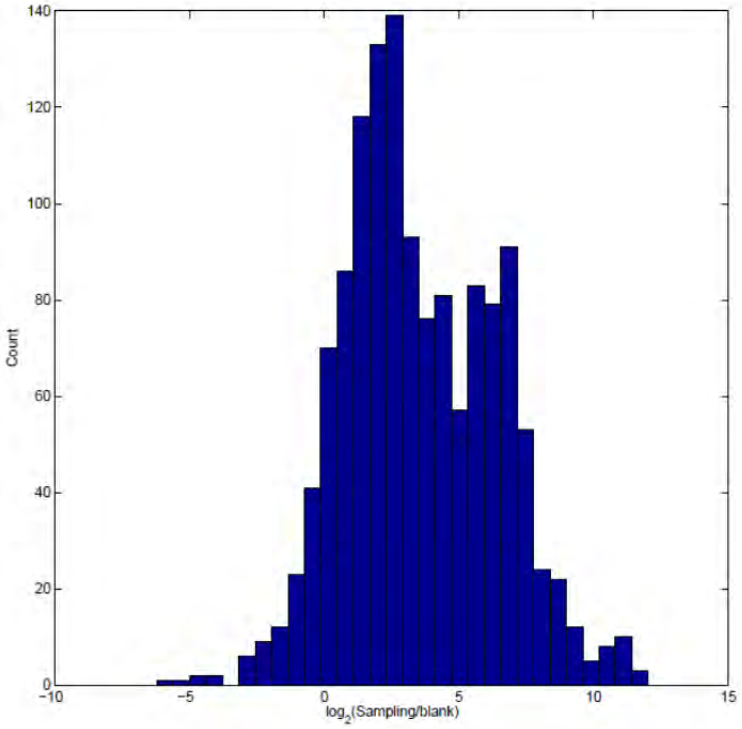

Figure 6: Distribution of Log_2 Ratios of Sample Concentrations/Blank Concentrations

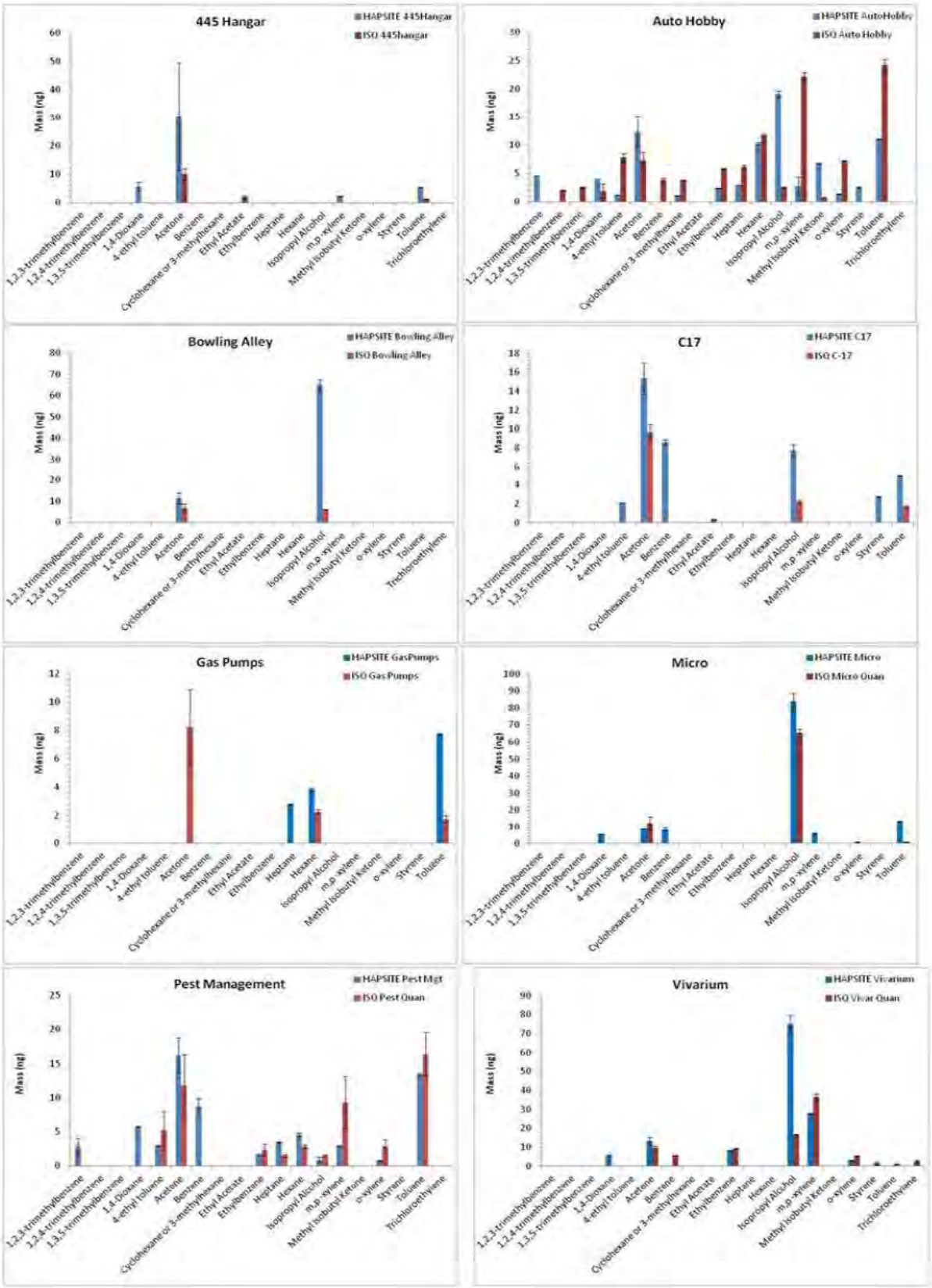

Figure 7: Comparison of Mass on tube for 8 Sites Sampled and Analyzed using HAPSITE and ISQ

5.0 CONCLUSIONS

This report assessed the accuracy of using passive VOC sampling as analyzed by lab methods and by the HAPSITE® ER for ambient air quality measurement. We have demonstrated a method for calculating mass on tube and calculating experimental and ideal uptake rates for passive thermal desorption tubes in HAPSITE® ER at various field sampling sites that could and should be used in actual field applications.

It is clear that compounds with published uptake rates can be sampled passively with the very simple methodology presented and still have a reliable result when analyzed with laboratory grade GC-MS system. That is a significant result given the low-level VOC concentrations found at the sites and that the TD system lends itself to very high throughput in collection and in analysis. This appears to be an ideal mechanism to allow assessment of ambient VOC levels at all locations, even if fully trained air sampling are not available or if the sampling needs outweigh the resource constraints of active sampling methods.

The performance of ISQ and HAPSITE® ER were evaluated by comparison of the calculated uptake rates for detected compounds at each site compared to the ideal (theoretical) and literature reported uptake rates. The ISQ data generated uptake rates for 12 of 18 detected compounds which were within 25% of the ideal uptake rates and/or uptake rates published in the literature, despite the fact that controlled laboratory settings were not applied to validate the uptake rates. In contrast, the uptake rates calculated from HAPSITE® ER were generally much lower than those reported by ISQ and compared to the ideal uptake rates, with only 1 of 15 compounds falling within 25% of the ideal uptake rate. We concluded that this is an instrumental problem, with the HAPSITE sensitivity of all samples with reported concentrations at low concentrations in question, and additionally misrepresenting the quantities of compound present on the trip blank because they were in the range of the apparent experimental limit of detection of the instrument. Specifically, any value below ~0.1 ppbv was reported as zero, resulting in higher ambient concentration calculations for each compound and lower uptake rates. Compounds also have different stabilities on the thermal desorption tube, and less-stable compounds may have been reduced to levels lower than the instrument sensitivity in HAPSITE® ER within the testing duration of 7-8 hours. Until this major challenge of sensitivity is resolved, the method for determining mass on tube and uptake rates may be validated (ISQ used the same method with experimental uptake rates generally within 25% of ideal uptake rates), but the values determined for HAPSITE are not likely to be as accurate as required. However, determining the mass on tube will be useful as a screening mechanism by the BE to identify the presence of an analyte in an area of suspected contamination until an active sample can be taken to better quantify concentration. While HAPSITE® ER did not perform as well as ISQ using the conditions in this study, there are several possible paths to improving passive sampling with HAPSITE® ER proposed in the next section.

6.0 RECOMMENDATIONS

In general, this study just focused on what compounds were present in the air in a variety of environments in the local community where significant exposures to highly hazardous compounds were not expected. VOC levels were relatively low so the analytical capabilities were stretched to the limits in terms of sensitivity. Also, no specific chemicals were targeted so methodology was not built to be more sensitive to any particular compound or types of compounds. So while the passive samples analyzed in the lab were successful, and the HAPSITE ER results were not as successful, it seems apparent that performing the work where more sample is able to be collected onto the media would make the HAPSITE much more likely to have positive results. To do this, sampling would either have to be longer for low level ambient samples, or could be used where higher levels are expected such as in industrial workplaces or more polluted locations such as in many of the military's deployed locations. Based on the results of this work, we provide the following specific recommendations:

- The BE career field should develop operational guidance to utilize this type of passive sampling for their health risk assessment needs. Using the published uptake rates with samples analyzed in the lab could be an extremely efficient way to collect a significant amount of exposure data at relatively low expense. Passively sampling for analysis in the field with the HAPSITE® ER will require further development but still appears to have tremendous benefits in situations where more mass can be collected on the media. This would be especially so if clear guidance can be given to the field on how to determine their own uptake rates in the setting they will be sampling in which should be a practical solution.
- A further step would be to develop fully validated methods for the most critical sampling scenarios that are expected in accordance to published guidance on how to do that (Markes 2012).
- Perform similar experiments to determine if increasing sampling time for passive collection provide better results and reduce variability (i.e., collected amount is above the HAPSITE® ER detection limit). This work was carried out with a seven to eight hour sampling time, but Markes provides separate results for uptake rates for workplace sampling (eight hours) versus environmental sampling (~four weeks) (Markes 2006). Increasing the sampling time may prove a valid option to improve passive HAPSITE® ER detection as long as the compounds are stable during the sampling period.
- Test whether spiking the TO-15 mix onto a replicate of the blank tubes at low levels (but above the limits of the system) would enhance instrumental sensitivity in a series of laboratory controlled experiments. If we know the profile of each compound with the spiked samples, we may be able to subtract out the spiked component to get a better estimate of the actual amount on the tubes. This will provide more accurate mass on tube and uptake rate calculations.
- Controlled laboratory analysis of uptake rates for the compounds reported in this study (as well as others relevant to the BE field) would be beneficial in further characterizing the field sampling environment. Markes recommends a combination of laboratory and field experiments (Markes 2012) to validate compound uptake rates. These experiments will provide a better idea of how accurate and

reproducible the ISQ and HAPSITE measurements really are under standardized conditions versus the field experiments compiled in this work. This would include studying the effect of temperature, pressure, and humidity data in future measurements.

- In lieu of having validated methods fully developed, one could deploy multiple trip blank tubes for each site, and/or characterize the concentrations of bleed compounds/artifacts present in multiple (10+) replicates of blank tubes. Statistical analysis of the multiple replicates will provide results as to the ideal number of trip blanks that should be deployed for field sampling. This will improve the confidence of a valid detection event in a field sample from a false positive (Section 4.4).
- A hardware and data storage issue resulted in a loss of data from one of the sampling sites analyzed with the HAPSITE® ER. A short analysis of the problem is that the HAPSITE® ER internal storage had reached its maximum limits, but a more detailed description of the issue can be found in the *HAPSITE® ER Field Sampling Report* (Kwak, et al.). The BE should be aware of this error, although it is highly unlikely that the field HAPSITE® ER will experience the same volume of samples as experienced in the laboratory setting. Inficon is also aware and is trying to remedy the problem.

7.0 REFERENCES

Bart, JCJ. "Direct Solid Sampling Methods for Gas Chromatographic Analysis of Polymer/Additive Formulations." *Polymer Testing*, 2001, 20, 729-740.

Batterman, Susan, et al. "Low-Flow Active and Passive Sampling of VOCs using Thermal Desorption Tubes: Theory and Application at an Offset Printing Facility." *J. Environ. Monit.*, 2002, 4, 361-370.

Harper, Martin. "Sorbent Trapping of Volatile Organic Compounds from Air." *J. Chrom. A.*, 2000, 885, 129-151.

Kwak, J., et al. *HAPSITE® ER Field Sampling Report*. DTIC (to be published, 2015).

Kwak, J., et al. *Evaluation of Potential Accessories to Support the HAPSITE® ER Thermal Desorption Capability*. DTIC (to be published, 2015).

Maddalena, Randy, et al. Measurement of Passive Uptake Rates for Volatile Organic Compounds on Commercial Thermal Desorption Tubes and the Effect of Ozone on Sampling. *LBL-6257E*. Ernest Orlando Lawrence Berkeley National Laboratory (May 2013)

Markes. Uptake Rates for Tube Type, Axial Diffusive Samplers, Thermal Desorption Technical Support No.1_8, 2006.

Markes. Principles of diffusive monitoring, Thermal Desorption Technical Support No. 8_4, 2012.

Markes. Use of Diffusive Samplers with Thermal Desorption – Capillary Analysis for Monitoring Volatile Organic Compounds (VOCs) in Ambient Air, Thermal Desorption Technical Support No. 10_4, 2009.

Martin, Nicholas, A. et al. "Verification of Diffusive and Pumped Samplers for Volatile Organic Compounds using a Controlled Atmosphere Test Facility." *Atm. Env.*, 2010, 3378-3385.

Roche, A., et al. "Performance of a Thermally Desorbable Type-Tube Diffusive Sampler for very Low Air Concentrations." *Atm. Env.*, 1999, 33, 1905-1912.

Sekiguchi H, Matsushita K,Yamashiro S, Sano Y,Seto Y, Okuda T, Sato A. "On-Site Determination of Nerve and Mustard Gases using a Field-Portable Gas Chromatograph-Mass Spectrometer." *Forensic Toxicol*, 2006, 24, 17-22.

Smith, P. "Person-Portable Gas Chromatography: Rapid Temperature Program Operation through Resistive Heating of Columns With Inherently Low Thermal Mass Properties." *J Chromatogr A* 2012, 1261 , 37-45.

8.0 LIST OF ABBREVIATIONS

AF	Air Force
AFB	Air Force Base
AFMS	Air Force Medical Service
AFRL	Air Force Research Laboratory
BE	Bioenvironmental Engineering/Engineer
bp	Boiling point
BTEX	Benzene, toluene, ethylbenzene, xylenes
EPA	Environmental Protection Agency
ER	Extended Range
GC-MS	Gas Chromatograph-Mass Spectrometer
HAPSITE	Hazardous Air Pollutants on Site
HRA	Health Risk Assessment
LC/MS	Liquid Chromatography/Mass Spectrometry
LESS	Logistically-Enabled Sampling System
LOR	Limit of Reporting
NEG	Non-Evaporative Getter
MS	Mass Spectrometry
SP	Smart Plus
SPME	Solid Phase Microextraction
SS	Stainless Steel
TD	Thermal Desorption
TWA	Time Weighted Average
USAFSAM	U.S. Air Force School of Aerospace Medicine
VOC	Volatile Organic Compound